

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

DEE, Ian, M.
Eric Potter Clarkson
Park View House
58 The Ropewalk
Nottingham NG1 5DD
ROYAUME-UNI

| | |
|--|--|
| Date of mailing (day/month/year) 22 March 2001 (22.03.01) | IMPORTANT NOTIFICATION |
| Applicant's or agent's file reference ICIM/P22915PC | |
| International application No. PCT/GB00/01861 | International filing date (day/month/year) 15 May 2000 (15.05.00) |

1. The following indications appeared on record concerning:

☒ the applicant

 ☐ the inventor

 ☐ the agent

 ☐ the common representative

Name and Address

IMPERIAL CHEMICAL INDUSTRIES PLC
Imperial Chemical House
Millbank
London SW1P 3JF
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person

 ☒ the name

 ☒ the address

 ☐ the nationality

 ☐ the residence

Name and Address

INEOS FLUOR HOLDINGS LIMITED
First Floor Offices
Queens Gate
15-17 Queens Terrace
Southampton
Hampshire SO14 3BP
United Kingdom

State of Nationality

State of Residence

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

ASSIGNMENT.

4. A copy of this notification has been sent to:

| | |
|---|---|
| <input checked="" type="checkbox"/> the receiving Office | <input type="checkbox"/> the designated Offices concerned |
| <input type="checkbox"/> the International Searching Authority | <input checked="" type="checkbox"/> the elected Offices concerned |
| <input checked="" type="checkbox"/> the International Preliminary Examining Authority | <input type="checkbox"/> other: |

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Peggy Steunenberg

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT ³

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

DEE, Ian, M.
Eric Potter Clarkson
Park View House
58 The Ropewalk
Nottingham NG1 5DD
ROYAUME-UNI

Date of mailing (day/month/year)
22 March 2001 (22.03.01)

Applicant's or agent's file reference
ICIM/P22915PC

International application No.
PCT/GB00/01861

IMPORTANT NOTIFICATION

International filing date (day/month/year)
15 May 2000 (15.05.00)

1. The following indications appeared on record concerning:

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Name and Address

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United Kingdom

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State of Residence
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Name and Address

INEOS FLUOR HOLDINGS LIMITED
First Floor Offices
Queens Gate
15-17 Queens Terrace
Southampton
Hampshire SO14 3BP
United Kingdom

State of Nationality

State of Residence

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:
ASSIGNMENT.

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☒ the elected Offices concerned
☒ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Peggy Steunenberg

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

| | |
|--|--|
| Date of mailing (day/month/year) 19 December 2000 (19.12.00) | |
| International application No. PCT/GB00/01861 | Applicant's or agent's file reference ICIM/P22915PC |
| International filing date (day/month/year) 15 May 2000 (15.05.00) | Priority date (day/month/year) 18 May 1999 (18.05.99) |
| Applicant GIBSON, Robin, Riyadh et al | |

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 29 November 2000 (29.11.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

| | |
|---|--|
| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35 | Authorized officer Zakaria EL KHODARY Telephone No.: (41-22) 338.83.38 |
|---|--|

PATENT COOPERATION TREATY

PCT

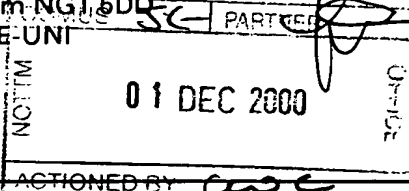
NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

DEE, Ian, M.
Eric Potter Clarkson
Park View House
58 The Ropewalk
Nottingham NG1 5DD
ROYAUME-UNI



| | | | |
|---|--|--|--|
| Date of mailing (day/month/year) 23 November 2000 (23.11.00) | | IMPORTANT NOTICE | |
| Applicant's or agent's file reference ICIM/P22915PC | | | |
| International application No. PCT/GB00/01861 | International filing date (day/month/year) 15 May 2000 (15.05.00) | Priority date (day/month/year) 18 May 1999 (18.05.99) | |
| Applicant IMPERIAL CHEMICAL INDUSTRIES PLC et al | | | |

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AG,AU,DZ,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW
The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).
3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 23 November 2000 (23.11.00) under No. WO 00/69797

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

| | |
|---|------------------------------------|
| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland | Authorized officer J. Zahra |
| Facsimile No. (41-22) 740.14.35 | Telephone No. (41-22) 338.83.38 |

Continuation of Form PCT/IB/308

**NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF
THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES**

| | |
|---|--|
| Date of mailing (day/month/year) 23 November 2000 (23.11.00) | IMPORTANT NOTICE |
| Applicant's or agent's file reference ICIM/P22915PC | International application No. PCT/GB00/01861 |
| <p>The applicant is hereby notified that, at the time of establishment of this Notice, the time limit under Rule 46.1 for making amendments under Article 19 has not yet expired and the International Bureau had received neither such amendments nor a declaration that the applicant does not wish to make amendments.</p> | |

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

DEE, Ian M.
Eric Potter & Clarkson
Park View House
58 The Ropewalk
Nottingham NG1 5DD
GRANDE BRETAGNE

| | |
|--------------|---------|
| DEE, Ian M. | PARTNER |
| 16 JUL 2001 | |
| ACTIONED BY: | |

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 13.07.2001

Applicant's or agent's file reference
ICIX/P22915PC

IMPORTANT NOTIFICATION

International application No.
PCT/GB00/01861

International filing date (day/month/year)
15/05/2000

Priority date (day/month/year)
18/05/1999

Applicant
INEOS FLUOR HOLDINGS LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Pfützner, G

Tel. +49 89 2399-8032



INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/GB 00/01861

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C17/087 C07C17/38 C07C17/383 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | EP 0 509 885 A (ATOCHEM ELF SA) 21 October 1992 (1992-10-21) the whole document | 1 |
| P,A | WO 99 26907 A (ICI PLC) 3 June 1999 (1999-06-03) cited in the application the whole document | 1-3,5 |
| P,A | WO 99 51555 A (DU PONT) 14 October 1999 (1999-10-14) claims | 1-4 |

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

5 October 2000

Date of mailing of the international search report

16/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/GB 00/01861

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 0509885 A | 21-10-1992 | FR 2675496 A | 23-10-1992 |
| | | AT 139513 T | 15-07-1996 |
| | | AU 650333 B | 16-06-1994 |
| | | AU 1497192 A | 22-10-1992 |
| | | CA 2065952 A | 18-10-1992 |
| | | ES 2088114 T | 01-08-1996 |
| | | GR 3020642 T | 31-10-1996 |
| | | JP 6135867 A | 17-05-1994 |
| | | MX 9201720 A | 01-10-1992 |
| | | US 5276225 A | 04-01-1994 |
| WO 9926907 A | 03-06-1999 | AU 1047799 A | 15-06-1999 |
| | | EP 1034157 A | 13-09-2000 |
| | | ZA 9810649 A | 25-05-1999 |
| WO 9951555 A | 14-10-1999 | AU 3377999 A | 25-10-1999 |

PCT

REC'D 17 JUL 2001

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| | | | |
|--|--|--|---|
| Applicant's or agent's file reference ICIX/P22915PC | FOR FURTHER ACTION | | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
| International application No. PCT/GB00/01861 | International filing date (day/month/year) 15/05/2000 | Priority date (day/month/year) 18/05/1999 | |
| International Patent Classification (IPC) or national classification and IPC C07C17/087 | | | |
| Applicant INEOS FLUOR HOLDINGS LIMITED et al. | | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

| | |
|---|--|
| Date of submission of the demand 29/11/2000 | Date of completion of this report 13.07.2001 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized officer Sen, A Telephone No. +49 89 2399 8328  |

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/01861

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

| | | | | |
|---------|---------------------|------------|----------------|------------|
| 1-3,7,9 | as originally filed | | | |
| 4-6,8 | as received on | 23/05/2001 | with letter of | 22/05/2001 |

Claims, No.:

| | | | | |
|-----|----------------|------------|----------------|------------|
| 1-8 | as received on | 23/05/2001 | with letter of | 22/05/2001 |
|-----|----------------|------------|----------------|------------|

Drawings, sheets:

| | |
|---------|---------------------|
| 1/4-4/4 | as originally filed |
|---------|---------------------|

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/01861

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | | |
|-------------------------------|------|--------|-----|
| Novelty (N) | Yes: | Claims | 1-8 |
| | No: | Claims | |
| Inventive step (IS) | Yes: | Claims | 1-8 |
| | No: | Claims | |
| Industrial applicability (IA) | Yes: | Claims | 1-8 |
| | No: | Claims | |

- 2. Citations and explanations**
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/01861

SECTION V:

D1: EP-A-0 509 885

D2: WO 99 26907 A

D3: WO 99 51555 A

The amendments made do not introduce subject-matter that was not present in the application as originally filed. In particular, the new claim 5 finds basis on page 4, lines 11 to 14. Renumbered claims 6 and 7 are dependent on the new claim 5. It is however clear from the text on page 4, lines 14 to 16 that additional hexafluoropropene (HFP) can be charged to the reactor or to the liquid phase separator.

The subject-matter of the present application directed to a process for the production of 1,1,1,2,3,3,3-heptafluoropropane (HFC 227ea) meets the requirements of Article 33(2) PCT since the prior art documents cited in the International Search Report do not describe the same preparation of HFC 227ea / separation of HFC 227ea from HF. D1 describes the separation of HF from 1,1,1-trifluoro-2-chloroethane. D2 describes the reaction between HFP and HF for the preparation of HFC 227ea. In particular, with regard to the separation of HFC 227ea from HF the document describes that the fluorine containing organic compound substantially free of hydrogen fluoride and the haloalkene/hydrogen fluoride azeotrope can be separated by charging the reaction product and the haloalkene to a distillation column and distilling the resulting mixture [D2: claim 1]. D3 describes a process for the separation of a mixture comprising HF and $\text{CF}_3\text{CClFCF}_3$.

The problem to be solved is the provision of an improved process for the production of HFC 227ea by improving the separation of HFC 227ea from HF. As discussed in the application HFC 227ea and HF as well as the ternary mixture of HF, HFC 227ea and HFP are known to form azeotropes and azeotrope-like mixtures which are difficult to separate by methods such as distillation.

This problem is solved according to the present application by charging the reaction mixture from the reaction of HFP and HF into a liquid phase separator so that two different phases can be separated. As shown in Example 1, the reaction mixture comprising HFC 227ea, HFP and HF spontaneously separates into two liquid phases, an organic phase and a HF phase in the liquid-phase separator [see also Table on

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/01861

page 9]. Such approach is not suggested in the cited prior art which deals or with different mixtures of compounds or with different solutions, e.g. distillation.

The requirements of inventive step under Art. 33(3) PCT appear accordingly to be met.

SECTION VII:

1. To meet the requirements of Rule 5.1(a)(ii) PCT, the documents D1 and D3 should be briefly identified in the description.
2. Claim 1 needs amendment with regard to the definition of HFP. Thus the expression "hexafluoropropane" should be corrected to read "hexafluoropropene".

The reaction mixture charged to the liquid-phase separator in Step A may be the mixture arising directly from the reactor in which HFP is reacted with hydrogen fluoride (direct mixture). It is often preferred, however, that the mixture charged to the liquid-phase separator is essentially an HFC 227ea/hydrogen fluoride azeotrope, for example obtained from distillation of the direct mixture.

It will be appreciated that the use of an HFC 227ea/HF azeotrope, or azeotrope-like mixture, in the process according to the present invention will not facilitate separation of the organic phase from the hydrogen fluoride-rich phase such use increases the amount of HFC 227ea to be removed per pass and, accordingly, reduces the amount of material to be recycled.

We have found surprisingly that addition of HFP facilitates separation of the HFC 227ea/hydrogen fluoride azeotrope into its components. The HFP may be introduced into the process according to the present invention at one or more appropriate points. For example, it may be charged to the reactor and/or to the liquid-phase separator in Step A and/or to the distillation column in Step C. Preferably the HFP is added to the liquid phase separator, either directly or mixed with the reaction mixture.

The reaction of HFP with hydrogen fluoride ~~in the process according to the first aspect of the present invention~~ may be carried out in the liquid phase or in the vapour phase.

To facilitate the separation in Step A of the process ~~according to the first aspect of the present invention~~, Step A is preferably carried out at below ambient temperature, typically at below 30°C.

To facilitate the separation in Step A of the process ~~according to the first aspect of the present invention~~, Step A is preferably carried out at supra-atmospheric pressure, typically 1-20 bars and preferably about 10 bars.

~~In a first embodiment of the process according to the first aspect of the present invention,~~ The product of the reaction of HFP with hydrogen fluoride ^{may be} distilled to recover a portion of the hydrogen fluoride therefrom before the mixture comprising HFC 227ea/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, HFP/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, and hydrogen fluoride is charged to the liquid phase separator in Step A.

The portion of hydrogen fluoride recovered by distillation in a recovery step prior to Step A, where such a recovery step is carried out, is preferably recycled to the reactor vessel.

5 ~~In a second embodiment of the process according to the first aspect of the present invention,~~ ^{Alternatively,} the product of the reaction of HFP with hydrogen fluoride ^{may be} charged directly to the liquid-phase separator in Step A.

Where HFC 227ea is prepared by reacting HFP with hydrogen fluoride in the ~~process according to the first aspect of the present invention in the~~ liquid phase in the presence of a catalyst, eg TaF_5 , NbF_5 or SbF_5 , it is suitably carried out at a temperature in 10 the range 20 to 200°C, preferably 40 to 120°C and especially 50 to 100°C. Suitably the reaction is carried out at superatmospheric pressure such that the reactants are in the liquid phase for sufficient time to react to produce HFC 227ea. Preferably the pressure is at least 5 bar and more preferably the pressure is 10 to 50 bar.

^A
15 ~~The residence time in the reactor in the process according to the first aspect of the present invention is~~ ^{is required} sufficient to permit conversion of HFP feedstock into HFC 227ea. The required residence time will be dependent on *inter alia* the degree of conversion required, the reactant ratio and the reaction conditions.

Where a low conversion rate of HFP into HFC 227ea is desired it is preferable that the feedstocks be recycled to increase the yield of HFC 227ea from the starting 20 material. However, we do not exclude the possibility that recycling is employed where high single pass conversions are required.

~~In the process according to the present invention~~ The molar ratio of hydrogen fluoride (HF) to HFP fed to the reactor is suitably at least 1:1 and preferably between 1.2 and 10:1. It will be appreciated that where a molar ratio of HF to HFP of 0.1 up to 1:1 is 25 employed the conversion ratio and/or the yield will be lower.

~~In the process according to the present invention~~ The molar ratio of HFP to the catalyst is suitably not more than 100:1 and is preferably between 1:1 and 50:1.

30 The levels of HF, HFP and catalyst in the process according to the present invention are suitably selected such that the catalyst and reactants are at least largely dissolved in the liquid phase under the reaction conditions employed.

The process according to the present invention may be operated in batch or continuous mode as desired. Semi-batch operation may also be employed in which one

or more feedstocks are fed continuously to the process and one or more other feedstocks are fed to the process in batch-wise fashion.

Alternatively, ^{reaction of HFP and HF} ~~the process according to the present invention~~ may be carried out in the vapour phase. Suitable conditions and catalysts for use in carrying out the ^{reaction} ~~process~~ ^{of HFP and HF} ~~according to the present invention~~ in the vapour phase are more fully described in DE 2712732 and GB 902590 mentioned hereinbefore.

The present invention will be further illustrated by reference to the accompanying drawings which illustrate, by way of example only, schematic representations of plants for carrying out the process according to the present invention.

10 In the drawings:

Figure 1 is a schematic representation of a plant wherein HFP is fed to the liquid-phase separator;

Figure 2 is a schematic representation of a plant wherein HFP is fed to the reactor;

Figure 3 is a schematic representation of a plant wherein the product of the reaction is
15 fed directly to the liquid-phase separator; and

Figure 4 is a ternary diagram illustrating HFC 227ea, HFP and HF separation.

In Figures 1 and 2, feed pipe (1) leads to a reactor (2), which optionally contains a fluorination catalyst. Product pipe (3) from the reactor (2) is in fluid-flow communication with a first distillation column (4), which is for example a single stage
20 flash vessel. Distillation column (4) is typically operated at a pressure of 12 bars with a bottoms temperature of 100°C and a tops temperature of around 50°C. Bottoms pipe (5) from distillation column (4) is in fluid-flow communication with feed-pipe (1). Tops line (6) from distillation column (4) is in fluid-flow communication with a liquid-phase separator (7). Tops line (8) from the liquid-phase separator (7) is in fluid-flow
25 communication with feed-pipe (1). Bottoms line (9) from the liquid-phase separator (7) is in fluid-flow communication with a second distillation column (10), which is for example a packed column. Distillation column (10) is typically operated at a pressure of around 12 bars with a tops temperature of 37°C and a bottoms temperature of around 60°C. Distillation column (10) is provided with an exit pipe for product (11) and a tops
30 pipe (12).

In Figure 1, tops pipe (12) from distillation column (10) is in fluid flow communication with tops line (6) which is provided with a feed-pipe (13).

unconverted HFP, often in the form of a ternary azeotrope, travels through product pipe (14) to the liquid-phase separator (7). HFP is fed via feed line (13) and product pipe (14) to liquid-phase separator (7). The liquid-phase separator (7) is typically operated at 0-20°C to afford better separation. In the liquid-phase separator (7), an HF-rich phase separates from the organics-rich phase. The HF-rich phase is returned via tops-line (8) to feed-pipe (1). The organics-rich phase flows via bottoms line (9) to distillation column (10). A stream comprising HFP and essentially all the hydrogen fluoride content of the stream entering distillation column (10) via line (9) is removed from the top of distillation column (10) via line (12) and returned to the liquid phase separator (7) via line (14). The product stream HFC 227ea is removed from the bottom of column (10) via exit pipe (11).

In the ternary diagram in Figure 4, compositions in the area of the figure designated A phase-separate, namely compositions comprising 0.4-0.6 mole % HF, greater than 0.4 mole % HFP and less than 0.6 mole % HFC 227ea. *fraction*

The present invention is further illustrated by reference to the following Examples.

Examples 1-4

These examples 1-4 illustrate the liquid-phase separation of HFP 227ea from HF and the enhanced separation thereof in the presence of HFP.

In the Examples, HFC 227ea and HFP, where used, were added to HF in a 500 ml whitey bomb cooled in liquid nitrogen. The whitey bomb was provided with a double-dip arrangement such that the dip-pipes would sample from the middle of each phase. The mixture was allowed to warm to room temperature, agitated, allowed to stand for 2 hours and then analysed.

The HF phase was analysed for organics by transferring a portion of the HF phase (10g) to a smaller whitey bomb containing water. It was allowed to stand for 15 minutes then the headspace was analysed by G.C.

The organics phase was analysed for HF by bubbling a portion of the organics phase through water scrubbers containing fresh de-ionised water and ice. The water was then analysed for fluoride.

The results are shown in the Table from which it can be seen that (a) a mixture of HFC 227ea and HF phase-separates such that an organic layer and an HF-rich layer are formed (Example 1) and (b) addition of HFP to the HFC 227ea/HF mixture reduces the

Claims

- 1,1,1,2,3,3,3-heptafluoropropane*
1. A process for the production of (HFC 227ea) by the reaction of (HFP) with hydrogen fluoride characterised by the Steps of *hexafluoropropane*
- 5 A. charging the reaction mixture from the reaction of HFP with hydrogen fluoride to a liquid-phase separator and allowing an organic phase and a hydrogen fluoride-rich phase to separate under gravity ;
- B. recycling the hydrogen fluoride-rich phase separated in Step A to the reactor in which the reaction is carried out;
- 10 C. charging the organic-rich phase separated in Step A to a distillation column;
- D. recovering the HFC 227ea and an hydrogen fluoride-rich mixture separately from the distillation column in Step (C); and
- E. recycling the hydrogen fluoride-rich mixture recovered from Step D to the reactor.
- 15 2. A process as claimed in Claim 1 wherein the reaction mixture charged to the liquid-phase separator in Step (A) comprises an HFC 227ea/HF azeotrope, or azeotrope-like mixture.
3. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at below
- 20 ambient temperature.
4. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at supra-atmospheric pressure
- 25 *6.* A process as claimed in Claim *5*, *wherein the additional* further characterised in that the HFP is charged to the liquid-phase separator.
- 7.* A process as claimed in Claim *5*, *wherein the additional* further characterised in that the HFP is charged to the reactor.
- 8.* A process as claimed in any one of the preceding claims wherein the mixture to be separated in the liquid-phase separator in Step (A) comprises a mole ratio of
- 30 HF:HFC 227ea of between 3:7 and 6:4.
5. A process according to any one of the preceding claims in which HFP in addition to that present in the reaction mixture from the reaction of HFP with hydrogen fluoride is introduced into the process.